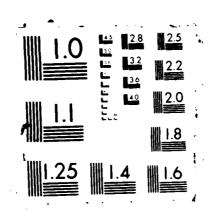
AD-R103 707 APPLICATIONS OF MULTIVALENT IONIC CONDUCTORS TO POLYMERIC ELECTROLYTE BATTERIES(U) MINNESOTA UNIV MINNEAPOLIS DEPT OF CHEMICAL ENGINEERING AND M.

UMCLASSIFIED J V CHERNG ET AL. JUL 87 N00014-85-K-0634 F/G 10/3 NL

END
9-81
0716





OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0634

R & T Code 413d019---01 Replaces Old Task # 627-850

TECHNICAL REPORT NO. 8



Applications of Multivalent Ionic Conductors To Polymeric Electrolyte Batteries

by

J.Y. Cherng, B.B. Owens, W.H. Smyrl, and M.Z.A. Munshi Department of Chemical Engineering and Materials Science University of Minnesota Minneapolis, MN 55455

Paper to be presented at 6th International Meeting on Solid State Ionics Garmisch-Partenkirchen September 6-11, 1987

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

ADAR3707

	REPORT DOCUM	MENTATION	PAGE			
1a. REPORT SECURITY CLASSIFICATION		I B. RESTRICTIVE	MARKINGS			
Unclassified				·		
LA SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION	Y Thierwiake /	OF REPORT		
25. DECLASSIFICATION / DOWNGRADING SCHEDULE		Unclassified/Unlimited				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		S. MONITORING ORGANIZATION REPORT NUMBER(S)				
ONE Technical Report #8						
6a. NAME OF PERFORMING ORGANIZATION	60. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION				
Corrosion Research Center	(11 application)	Office of Naval Research, Resident Rep.		dent Rep.		
∠ ∆OORESS (City, State, and ZIP Code)		75. ADDRESS (City, State, and ZIP Code)				
University of Minnesota		Federal Building, Room 286				
Minneapolis, MR 55455		536 South Clark Street Chicago, IL 60605-1588				
32. NAME OF FUNDING, SPONSORING ORGANIZATION	35. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		REBMUN		
Office of Waval Research	Code 1113	Contract	No. N00014	-85-₹-0634	1 :	
3c. ADORESS (City, State, and ZIP Code)		10. SOURCE OF				
800 North Qunicy Street		PROGRAM	PROJECT	TASK	WORK UNIT	
Arlington, VA 22217-5000		ELEMENT NO.	NO.	NO.	ACCESSION NO.	
11. TITLE (Include Security Classification)		<del></del>	. <del></del>	<u>-</u>		
Applications of Multivalent Id	onic Conductors	to Polymeric	Electroly	te Batteri	es	
12. PERSONAL AUTHOR(S)		·				
J.Y. Cherne, B.R. Owens, W.H.	Smarl M 7 A M	wachi			, ,	
13a. TYPE OF REPORT 13b. TIME C		14. DATE OF REPO		n, Oay) 15. PA	GE COUNT	
16. SUPPLEMENTARY NOTATION				<u> </u>	:	
Paper to be presented at the (	th Internationa	l Meeting or	solid Sta	te Ionics.	Garmisch-	
Partenkirchen, September 6-						
17 COSATI CODES	18. SUBJECT TERMS	Continue on reven	se if necessary a	ina identity by	plack number)	
FIELD   GROUP   SUB-GROUP	divalent con	nductors. 📻	imnedan	ce cells	\no!vmer	
<del>\\\\</del>	electrolyte	menue	/ -		poryaer .	
	- Crecerory ee.	3 4 WEZ	im LEAN	2/2/7/	Vites VANABIUM	
Fast ion conduction has been			1			
alkali metal salt. Recently of						
ionically conducting polymers.	. Certain compl	exes\(namels	the Mo <sup>2+</sup>	based) wer	e found to be	
anion conductors while others,	(namely the Pb2	+ based we	e cation c	onductors.	Tein	
therefore of interest to study	the reasons fo	r the appare	ent differe		conductivity	
measurements are currently be	ing evaluated on	a number of	E polymer d	livalent sa	lt complexes.	
Electrochemical cells are bein	ng constructed w	ith appropri	ate cathod	les to asse	ss the	
feasibility of these polymer of			e batteries	One suc	h design	
	lg/(PEO) <sub>4</sub> ·Mg(ClO				2014.72 () S	
has an open circuit voltage of	zv and a theor	etical energ	y density	ot 346 Wh/	kg.	
Performance of large scale bat	lerres may be d	erived irom	tne protot	ype cell s	tuales.	
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT		21 ABSTRACT	ECLAITY CLASS	FICATION		
SEUNCLASSIFIEDAUNUMITED SAME AS						
224 NAME OF RESPONSIBLE MOIVIOUAL		225. TELEPHONE	Unclude Area C	oger ( IZC OFFIC	E SYMBOL	
Boone B. Owens		(612) 62	5-1332		·	

DD FORM 1473, 34 MAR

All other editions are dosolete.

SECURITY CLASSIFICATION OF THIS PAGE

# APPLICATIONS OF MULTIVALENT IONIC CONDUCTORS TO POLYMERIC ELECTROLYTE BATTERIES

J.Y. Cherng B.B. Owens W.H. Smyrl M.Z.A. Munshi

Department of Chemical Engineering and Materials Science
Corrosion Research Center
University of Minnesota
221 Church St. SE
Minneapolis, MN 55455

Fast ion conduction has been demonstrated in certain polymer materials doped with an alkali metal salt[1]. Polyethylene oxide (PEO) has been the most widely used polymer. It was found that PEO doped with a lithium salt such as  $\text{LiCF}_3\text{SO}_3$  could give conductivity values of about  $10^{-4}$  at  $100^{\circ}\text{C}[2]$ . The transport number of the Li<sup>+</sup> ion in these complexes has been found to be less than one. Despite this, the application of polymer electrolytes to solid state batteries has aroused considerable interest worldwide. The main attractive features such as high energy density, ease of fabrication of the battery components, variable geometry and long shelf life have led to proposed applications spanning across the whole battery product range from microelectronics to electric vehicle.

Cells utilizing the monovalent salt-polymer electrolyte, alkali metal anodes and cathodes based on insertion compounds have demonstrated good cycling and good reversibility at 100°C. Attempts have also been made to improve the conductivity of these polymer electrolytes by appropriate modifications for ambient temperature solid state batteries.

ŚŚŚŚŚŚŚ∮∱ŚŚŚŚŚŚ¶¶DDZOZOZ¶BSSSSZ¶PSSSZERPSSSZ¶ ROSOSOZ¶ KOŚŚŚŚŚ U PRZYSZZZZZZZZ

Recently divalent salts have also been used in the preparation of ionically conducting polymers [3,4]. Certain complexes (namely the  $Mg^{2+}$  based) were found to be anion conductors while others (namely the  $Pb^{2+}$  based) were cation conductors. It is therefore of interest to study the reasons for the apparent difference. A.c. conductivity measurements are currently being evaluated on a number of polymer divalent salt complexes. Electrochemical cells are being constructed with appropriate cathodes to assess the feasibility of these polymer electrolytes in rechargeable batteries. One such design

Mg |  $(PEO)_4 \cdot Mg(ClO_4)_2 | V_6O_{13}$  has an open circuit voltage of 2V and a theoretical energy density of 346 Wh/kg. Performance of large scale batteries may be derived from the prototype cell studies.

### References

- [1] B.E. Fenton, J.M. Parker and P.V. Wright, Polymer, <u>14</u>, 589 (1973).
- [2] M.B. Armand, J.M. Chabagno and M.J. Duclot, in "Fast Ion Transport in Solids," Eds. P. Vashista, J.N. Mundy and G.K. Shenoy, p. 131, (North-Holland, New York 1979).
- [3] L.L. Yang, A.R. McGhie and G.C. Farrington, submitted for publication.
- [4] R.Hug, G. Chiodelli, P. Ferloni, A. Magistris and G.C. Farrington, J.Electrochem. Soc. <u>134</u>, 364 (1987).

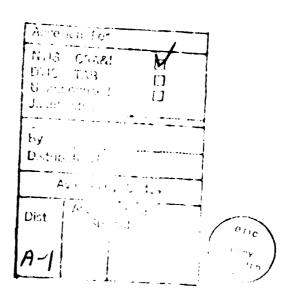
### Acknowledgements

This work was supported in part by the Office of Naval Research and the Department of Energy.

# QL/1113/87/2

# TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 1911	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1



#